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Mark L. Dietz,¹ Paul G. Rickert,¹ Mark R. Antonio,¹ Millicent A. Firestone,²
James F. Wishart,³ and Tomasz Szreder³

¹*Chemical Sciences and Engineering and* ²*Materials Science Divisions, Argonne National Laboratory, Argonne, IL 60439.* ³*Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973. Corresponding author email address: mdietz@anl.gov*

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Chemistry Department

Brookhaven National Laboratory

P.O. Box 5000
Upton, NY 11973-5000
www.bnl.gov

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Mark L. Dietz,¹ Paul G. Rickert,¹ Mark R. Antonio,¹ Millicent A. Firestone,²
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¹*Chemical Sciences and Engineering and* ²*Materials Science Divisions, Argonne National Laboratory, Argonne, IL 60439.* ³*Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973. Corresponding author email address: mdietz@anl.gov*

ABSTRACT

The pairing of a Lindqvist or Keggin polyoxometalate (POM) anion with an appropriate tetraalkylphosphonium cation, $[R_3R'P]^+$, has been shown to yield an original family of ionic liquids (POM-ILs), among them salts liquid at or near ambient temperature. The physicochemical properties of several such “inorganic liquids”, in particular their thermal properties, suggests the possible application of these compounds as robust, thermally-stable solvents for liquid-liquid extraction. A preliminary evaluation of the potential of POM-ILs in this application is presented.

INTRODUCTION

Growing recognition of the need to devise more environmentally friendly chemical processes and to extend the principles and practices of “green chemistry” to chemical separations has recently led to a substantial increase in interest in ionic liquids (ILs), particularly those that are liquids at ambient temperature (designated “room temperature ionic liquids” or RTILs), as alternatives to conventional organic diluents in various solvent extraction processes [1]. Many ionic liquids exhibit a variety of unique and interesting properties that make them promising in such applications, including low flammability, good thermal stability, and a near-absence of vapor pressure. In contrast to ordinary organic diluents, ionic liquids are also extraordinarily tunable solvents, with even the slightest changes in the structure of the anionic or cationic components frequently leading to substantial alterations in physicochemical properties [2]. Despite recent studies indicating that the use of various common ionic liquids (*e.g.*, N, N'-dialkylimidazolium salts) in combination with certain well-known neutral extractants (*e.g.*, crown ethers) may prove problematic [3], other work suggests that the unique solvation environment afforded by these liquids may offer new opportunities for the design of novel separations [4].

With this in mind, we have been exploring the properties and potential applications of an as yet small, but potentially significant sub-class of ILs, “inorganic

liquids”[5], in which one component of the IL consists of a metal oxide cluster [6], a silica nanoparticle [7], or other similar inorganic moiety. Recent work in This Laboratory has concerned the possibilities afforded by inorganic liquids comprising combinations of a polyoxometalate anion (*e.g.*, Keggin, Lindqvist) and tetraalkylphosphonium cations [8, 9]. In this report, we summarize the characteristics of these materials relevant to their potential application as solvents in liquid-liquid extraction and present preliminary data concerning the application of one of them as an extraction solvent.

EXPERIMENTAL

Preparation of ILs

Trihexyl(tetradecyl)phosphonium bromide was obtained as a generous gift from Cytec Canada, Inc. (Niagra Falls, Ontario) and used without further purification. All other materials were reagent grade and unless noted otherwise, were used as received. Lindqvist-based ($W_6O_{19}^{2-}$) ILs were prepared from sodium tungstate by the method of Klemperer [10], modified by substitution of a tetraalkylphosphonium bromide for the corresponding tetraalkylammonium salt. The analogous Keggin heteropolytungstate ($[PW_{12}O_{40}]^{3-}$) salts were prepared by reaction of $H_3PW_{12}O_{40}$ with a tetraalkylphosphonium bromide under the same conditions. Addition of absolute methanol to the reaction mixture led to precipitation of the product, which following methanol and diethyl ether washes, was dried at 80 °C for 24 hours. Product purity was confirmed by NMR, elemental analysis, and high-resolution FAB-MS.

Characterization of ILs

Viscosity measurements.

A Cambridge Applied Systems ViscoLab400 reciprocating piston viscometer equipped with a flow-through jacket for temperature control was used for all viscosity measurements. Temperature control was achieved using a Lauda Proline RP-845 circulating bath. Placement of the viscometer head in an N_2 -purged acrylic box eliminated absorption of atmospheric moisture by the samples.

Thermal property measurements.

For differential scanning calorimetry (DSC), 5-10 mg aliquots of the IL of interest were sealed in Al pans and equilibrated at -75 °C for 5 minutes before the start of the heating cycle. Data were collected using a scan rate of 2 °C/min. Calibration of the instrument, a TA Instruments model Q100 equipped with a refrigerated cooling system, was performed using an indium standard. For thermogravimetric analyses (TGA), a TA Instruments Q50 was employed. In a typical run, a weighed portion (2-5 mg) of sample was heated in a Pt pan from 25-600 °C at a rate of 10 °C/min under nitrogen flow.

Distribution ratio measurements.

All distribution ratios were determined radiometrically. Specifically, aliquots (500 μ L) of the organic phase were pre-equilibrated *via* two contacts with twice their

volume of an appropriate nitric acid solution. A portion of each pre-conditioned organic phase was then combined with an equal volume of an appropriate uranium (^{233}U)-spiked aqueous phase. Following a period (30-60 min.) of intermittent of vortex mixing, the mixture was centrifuged until phase separation was complete. Two 50 μL aliquots of each phase were then withdrawn for analysis by liquid scintillation counting on a Packard Model 2200CA Liquid Scintillation Analyzer.

RESULTS AND DISCUSSION

Among the most important of the variety of parameters that determine the suitability of a particular solvent for application in liquid-liquid extraction are its physical/chemical stability and viscosity, along with the efficiency of extraction of the metal ion(s) of interest afforded by the solvent. Prior work in a number of laboratories indicates that ionic liquids, while often more viscous than conventional organic solvents, offer the advantages of higher extraction efficiency [4] and excellent physical, thermal, and radiolytic stability [11-14]. Our efforts to evaluate the utility of inorganic liquids as extraction solvents began with an examination of the extraction of uranium by tri-*n*-butyl phosphate (TBP) into *bis*[trihexyl(tetradecyl)phosphonium][W_6O_{19}]. Figure 1 shows the nitric acid dependency of D_{U} obtained for a “PUREX-like” process solvent comprising a 1.2 M solution of TBP in this Lindqvist IL. Also shown for purposes of comparison are the results obtained for the same concentration of the extractant in dodecane and in a “traditional” ionic liquid, 1-pentyl-3-methylimidazolium *bis*[(trifluoromethyl)sulfonyl]imide ($\text{C}_5\text{mim}^+\text{Tf}_2\text{N}^-$).

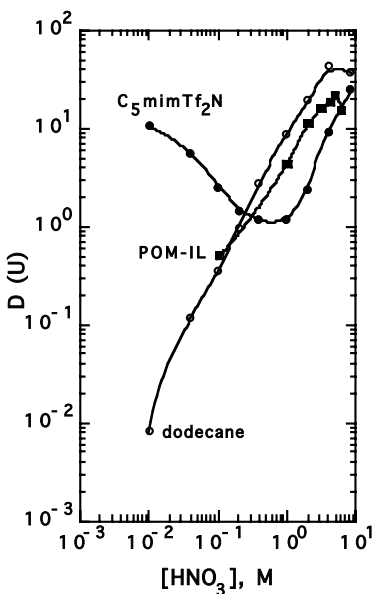


Figure 1. Nitric acid dependency of D_{U} for dodecane and two ionic liquids ($T = 22\text{ }^{\circ}\text{C}$)

As can be seen, in contrast to the relatively hydrophilic, imidazolium-based IL, which exhibits a complex dependency of D_{U} upon nitric acid concentration (the result of the gradual replacement of partitioning *via* an ion-exchange process by extraction of a neutral uranyl nitrato-TBP complex), the nitric acid dependency of D_{U} for the POM-IL closely

resembles that observed for dodecane. As has been noted previously in studies of the partitioning of various metal ions into $C_n\text{mim}^+\text{Tf}_2\text{N}^-$ ILs in the presence of neutral extractants, as the hydrophobicity of the cation comprising an IL is increased, the acid dependency of D_M observed increasingly resembles that observed for conventional organic solvents (in which D_M rises with increasing acidity) [15]. Thus, it is not unexpected that the Lindqvist IL, which incorporates a comparatively hydrophobic phosphonium cation, would exhibit an acid dependency of D_U similar to that of the hydrocarbon solvent. It is important to note, however, that at any given acidity, the uranium distribution ratio observed for the POM-IL is actually lower (by *ca.* a factor of 2) than that observed for dodecane, a result which clearly calls into question the notion of the superiority of ILs over conventional diluents as extraction solvents [4]. Nonetheless, the values of D_U observed are more than adequate for purposes of devising a workable POM-IL-based extraction system.

In the course of efforts to measure uranium extraction into the Lindqvist IL, it became apparent that this solvent is inconveniently viscous, despite the presence of nearly 40% (v/v) TBP. For this reason, we next examined the temperature-dependence of the viscosity of the Lindqvist IL and, for purposes of comparison, the analogous bromide salt. Figure 2 shows the results obtained, presented as plots of the dependence of the viscosity on reciprocal temperature.

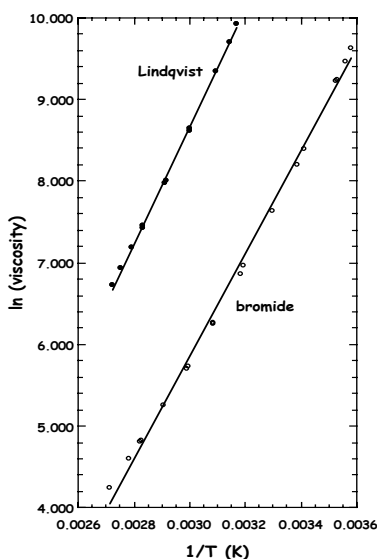


Figure 2. Temperature dependence of viscosity for two tetraalkylphosphonium ILs

Although the Arrhenius-like behavior of the temperature dependence is interesting from a fundamental point of view, of more importance from a practical perspective are the IL viscosities over the range of temperatures that might be encountered in an extraction process (*ca.* 20-90 °C). It is readily evident that over much of this range, the viscosities are quite high; at temperatures less than 40 °C, in fact, the viscosity of the Lindqvist IL exceeds the working range of the viscometer employed (20,000 mPa.s) and is estimated to approach 75,000 mPa.s at room-temperature, although

the steep temperature-dependence means that by 90 °C, the viscosity falls to less than 1000 mPa·s. (While the viscosities of related ILs incorporating smaller cations or anions, such as the analogous bromide salt (shown), are typically much lower, the not insignificant water solubility of many of them precludes their use as extraction solvents.) If these results prove to be representative of typical inorganic liquids, their application at near-ambient temperatures in a conventional liquid-liquid mode is likely to be problematic.

Given the steep decline in the viscosity of the Lindqvist IL that accompanies rising temperature, it seems reasonable to expect that if inorganic liquids do find application in extraction processes, it will be at elevated temperatures. For this reason, some consideration of the thermal properties (in particular, the stability) of these compounds is important. Differential scanning calorimetry on the Lindqvist IL revealed no primary transitions over the range of temperatures studied (up to 100 °C), only a glass transition at -48 °C. Results for the analogous Keggin-based IL were similarly straightforward, revealing only the presence of a melting point at 65 °C (thus indicating that the substitution of a Keggin anion for the Lindqvist ion would do nothing to improve the viscosity results shown in Figure 2). In neither case was any evidence of decomposition noted. Because prior studies concerning the relationship between IL structure and physicochemical properties have noted that for a given cation, there exists an approximately inverse relationship between anion nucleophilicity and the IL decomposition temperature [16], ILs comprising phosphonium cations and bulky, charge-diffuse anions such as POMs should exhibit excellent high-temperature stability. In fact, thermogravimetric analyses indicate that the onset of decomposition of the *tris*[trihexyl(tetradecyl)phosphonium] Keggin and the corresponding Lindqvist ILs does not occur until 456 °C and 482 °C, respectively, more than 100 °C above the decomposition of the analogous bromide IL. Isothermal gravimetric measurements, in which the Lindqvist IL showed no decomposition while held at 360 °C for several hours, lead to the same conclusion: that POM-based ILs exhibit excellent thermal stability.

CONCLUSIONS

The preliminary results presented here provide a mixed picture concerning the potential utility of POM-based ionic liquids as extraction solvents. Despite exhibiting excellent thermal stability and yielding uranium extraction efficiencies approaching those observed for a conventional organic solvent in the presence of TBP, the “inorganic liquids” considered are highly viscous at ambient temperature. Systematic studies of the influence of co-solvents and extractants on POM-IL viscosity and of alternative configurations (*e.g.*, supported liquid membranes) for employing these solvents are clearly needed if the possibilities afforded by these unique materials as extraction solvents are to be realized. Work addressing these opportunities is now underway in This Laboratory.

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